

LEO DEGRADATION OF GRAPHITE AND CARBON-BASED COMPOSITES ABOARD
SPACE SHUTTLE FLIGHT STS-46*

Blaine R. Spady

R.A. Synowicki

Jeffrey S. Hale

M.J. DeVries

John A. Woollam

Center for Microelectronic and Optical Materials Research, and Department of Electrical
Engineering, University of Nebraska-Lincoln

Lincoln, NE 68588-0511

Phone: 402/472-1978, Fax: 402/472-7987

Arthur W. Moore

Union Carbide Corporation, Parma Technical Center

Parma, Ohio

Max Lake

Applied Sciences, Incorporated

Cedarville, Ohio

SUMMARY

Six different types of carbon and carbon-boron nitride composites were exposed to low Earth orbit aboard Space Shuttle flight STS-46. The samples received a nominal atomic oxygen fluence of 2.2×10^{20} atoms/cm² in 42 hours of exposure. Pyrolytic graphite and highly oriented pyrolytic graphite showed significant degradation, and the measured erosion yield was within a factor of two of published values. The erosion yield of pyrolytic boron nitride was found to be 2.6×10^{-26} cm³/atom in plasma asher exposure, over 42 times lower than that of pyrolytic graphite. This low erosion yield makes graphite plus boron nitride mixtures quite resistant to low earth orbit exposure. Evidence suggests that the graphitic component was preferentially etched, leaving the surface boron nitride rich. Degradation resistance increases with boron nitride composition. Carbon fiber/carbon composites degraded in low Earth orbit, and the carbon pitch binder was found to etch more easily than the graphite fibers which have much higher degradation resistance.

*Research Supported by NASA-Lewis Research Center Grant NAG-3-95

INTRODUCTION

High temperature radiators are necessary for rejection of waste heat generated aboard orbiting spacecraft (refs. 1,2). Radiator materials must be able to operate at temperatures up to 900 K. Other materials requirements for space radiators are high thermal conductivity and surface emittance. Furthermore, conductivity and emittance must not change with exposure to the corrosive low Earth orbit (LEO) space environment.

Atomic oxygen (AO) is the primary reactive species present in LEO (ref. 3). Oxygen atoms strike spacecraft surfaces with an average kinetic energy of 4.5 eV due primarily to the orbital speed of the spacecraft. The AO attack is directional along the spacecraft's velocity vector since the spacecraft is moving into the oxygen atoms. Ultraviolet light from the sun is also present and synergistic degradation effects are suspected.

Ion beams have been extensively used to modify the surface morphology of many materials, resulting in a "carpet-like" surface texturing (ref. 4). Surface modification of this type can significantly alter the surface emittance of a waste heat radiator.

Bulk basal plane pyrolytic graphite, as well as vapor grown carbon fibers, shows the highest thermal conductivity of all materials (ref. 5). Also, graphite can withstand temperatures up to 2800 K and has found extensive use in high temperature applications. These properties make graphite an excellent choice for radiator applications. However, it has been shown in both laboratory simulations and actual LEO exposure that graphite is readily etched by AO (ref. 6).

This paper considers the AO degradation resistance of six different types of graphite, graphite plus boron nitride mixtures, and carbon fiber/graphite composites. Their usefulness as space radiator materials has been evaluated through exposure to LEO aboard Space Shuttle flight STS-46 in July 1992.

EXPERIMENT

Six different types of materials were prepared in bulk form. Two different types of graphite were chosen, namely pyrolytic graphite (PG) and highly oriented pyrolytic graphite (HOPG) (ref. 5). Two samples consisted of carbon and boron nitride mixtures (C-BN). These two C-BN samples consisted of one hot-pressed and one as-deposited containing 40% and 60% pyrolytic graphite, respectively (ref. 7). It will be shown that the presence of boron nitride in the mixture serves to greatly decrease erosion. Boron nitride is not as good a thermal conductor as graphite, so the thermal conductivity of C-BN materials is less than that of pure graphite, but should still be quite acceptable for space radiator applications.

The remaining two samples were composites of vapor grown carbon fibers embedded in a graphite (pitch) matrix. These carbon/carbon fiber (C/C) composites were made by either liquid or gas infiltration of the graphite precursor into the fiber weave.

Sample characterization consisted of accurate measurements of mass and dimensions. Mass was measured using an ultramicrobalance with a resolution of 10^{-7} g and the physical dimensions were measured using a vernier caliper with a resolution of 25 μm . Dimension and mass measurements allow for measurement of erosion yield (ref. 6).

Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were employed to measure topographic changes and quantify surface roughness. The AFM is a contact method which gives extremely fine scale measurements of surface roughness over small areas, on the order of 100 μm or less.

The bulk samples were cut into circular geometries to fit into the provided sample holder. In order to isolate the effects of the AO, the back sides of the samples were used as control surfaces.

All samples were part of the limited duration space environment candidate materials exposure-3 payload, aboard STS-46. The samples were exposed to the space environment throughout the entire shuttle flight. However, the samples received direct ram exposure to AO for only 42 hours during the 8-day mission and the oxygen fluence received during this exposure was nominally 2.2×10^{20} atoms/cm². Oxygen fluence was determined by both atmospheric modeling using the MSIS-86 thermospheric model (ref. 8) and by a mass spectrometer flown aboard STS-46 on the EOIM-3 payload. Kapton[®] mass loss measurements (ref. 9) showed the oxygen fluence to be 2.3×10^{20} atoms/cm².

RESULTS AND DISCUSSION

The PG, HOPG, and C/C composites all showed visible degradation. This is shown in Fig 1. The C-BN samples showed no visible degradation except for a slight "darkening" of the 60% C-BN sample.

SEM results for the PG, HOPG, and C/C composite made by gas infiltration showed uniform degradation. The C/C composite made by liquid infiltration showed preferential degradation of the graphite pitch surrounding the carbon fibers as shown in Fig 2. The 40% C-BN sample showed no changes in the SEM photos.

The hot-pressed 40% C-BN sample is comprised of microscopic domains of pure pyrolytic boron nitride and boronated PG; the size of the domains was found to slightly exceed 0.1 μm . Evidence on the as-deposited 60% C-BN was inconclusive of whether or not the material is a single-phase mixture of C, B, and N or a two-phase mixture of pyrolytic boron nitride domains and boronated PG domains (ref. 7). Fig 3 shows an unexposed and exposed AFM picture of the surface of the 60% C-BN sample. The figure appears to show the preferential etching of either

PG or pyrolytic boron nitride domains. A preliminary study of pyrolytic boron nitride using oxygen plasma ashers showed the erosion yield to be $2.6 \times 10^{-26} \text{ cm}^3/\text{atom}$. This is over 42 times lower than the published $1.1 \times 10^{-24} \text{ cm}^3/\text{atom}$ erosion yield of PG (ref. 6). This suggests that the PG is being preferentially etched, leaving pyrolytic boron nitride domains. This behavior was observed in both the as-deposited and hot-pressed materials. Table I shows the surface roughness data for the 40% and 60% C-BN samples taken for three scan sizes with the AFM. The $1 \mu\text{m}$ scan has the greatest percentage change between the unexposed and exposed samples; namely, 59% for the 40% C-BN, and 238% for the 60% C-BN samples. The percentage change for the $100 \mu\text{m}$ scan was only 29% for the 40% C-BN and 36% for the 60% C-BN. This indicates the surface roughened on a sub micron scale, for which the small scans were more sensitive. From this data it can be seen that the 40% C-BN sample was more stable in LEO than the 60% C-BN sample; this is to be expected since pure pyrolytic boron nitride has a lower erosion yield than PG.

Table I. RMS Surface Roughness of 40% and 60% C-BN

SAMPLE	AFM 1 μm scan	AFM 10 μm scan	AFM 100 μm scan
40% C-BN unexposed	9.88 nm	56.714 nm	108.500 nm
40% C-BN exposed	15.713 nm	70.460 nm	139.600 nm
60% C-BN unexposed	9.343 nm	15.619 nm	133.137 nm
60% C-BN exposed	31.586 nm	37.377 nm	181.667 nm

The densities (ρ) of the samples were determined from the physical dimensions and mass. The mass loss (ΔM) of each sample was the pre-flight mass minus the post-flight mass. The AO fluence (F) was nominally $2.2 \times 10^{20} \text{ atoms/cm}^2$. The erosion yield was calculated as:

$$\epsilon = \frac{\Delta M}{\rho A F}$$

where A was the exposed area of the sample. The mass loss, density, and erosion yield for all samples are shown in Table II. The densities and erosion yields of the PG and HOPG samples were within a factor of two of published data (ref. 6). The C/C composites and C-BN samples were new materials in space so there were no published data for comparison. The erosion yields for the C-BN samples were an order of magnitude lower than either the PG or the HOPG. The gas infiltrated C/C composite erroneously lost mass due to handling, making the data unusable.

The degradation observed on pure graphite samples and the pitch in C/C composites indicates that these materials are not stable in LEO and will require protective coatings if deployed. The degradation resistance of C-BN mixtures is very encouraging. These materials

show promise as radiator materials without the need for protective overcoats due to the presence of boron nitride. The sample containing 40% carbon outperformed that containing 60% carbon. Much more work could be done studying the effectiveness of bulk mixtures of carbon and boron nitride, as well as graphite fiber composites containing boron nitride in the binding matrix. Fiber composites of this type would be advantageous since the thermal conductivity would be dominated by the graphite fibers, and atomic oxygen resistance would be enhanced by the presence of boron nitride.

Table II. Measured Density, Mass Loss, and Calculated Erosion Yield for all Samples

Material	Density (g/cm ³)	Mass Loss (mg)	Erosion Yield (cm ³ /atom)
PG	2.171	.62	.538x10 ⁻²⁴
HOPG	2.096	.77	.692x10 ⁻²⁴
40% C-BN	2.134	.08	.071x10 ⁻²⁴
60% C-BN	1.782	.21	.222x10 ⁻²⁴
C-C Liquid Infiltration	1.403	.22	1.093x10 ⁻²⁴
C-C Gas Infiltration	1.517	11.5398	*****

CONCLUSION

Six different carbon based materials were exposed to 42 hours of LEO aboard Space Shuttle flight STS-46. The PG, HOPG, and C/C composites were degraded by AO exposure, making them less desirable for space radiator applications. Measured erosion yields agreed well with published results. Samples of C-BN showed a strong resistance to atomic oxygen erosion. This resistance increased as the percentage of carbon decreased since the erosion yield of pyrolytic boron nitride is lower than that of PG by a factor of 42. In these C-BN mixtures, atomic oxygen preferentially etches the graphitic component of the material at the surface, leaving the surface boron nitride rich. C/C composites degraded easily when exposed to LEO. The graphite binder eroded similarly to bulk pyrolytic graphite; however, graphite fibers in the C/C composites were found to erode much more slowly than the surrounding pitch binder.

REFERENCES

1. Mirtich, Michael J., Kussmaul, Michael T., Enhanced Thermal Emittance of Space Radiators by Ion-Discharge Chamber Texturing, NASA TM-100137, March 1987.
2. Rutledge, Sharon K., Banks, Bruce A., Mirtich, Michael J., High Temperature Radiator Materials for Applications in the Low Earth Orbital Environment, NASA TM-100190, April 1987.
3. U.S. Standard Atmosphere 1976, U.S. Government Printing Office, NASA TM-X-74335, 1976.

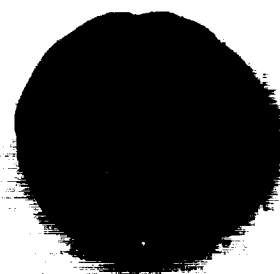
4. Banks, Bruce A., Ion Beam Applications Research- A 1981 Summary of Lewis Research Center Programs, NASA TM-81721, April 1981.
5. A.W. Moore, "Highly Oriented Pyrolytic Graphite," in Physics and Chemistry of Carbon, Volume 11, Edited by Philip L. Walker Jr. and Peter A. Thrower, Marcel Dekker, Inc., New York, 1973, pp 69-185.
6. Banks, Bruce A., Rutledge, Sharon K., and Brady, Joyce A., "The NASA Atomic Oxygen Effects Test Program," Proceedings of the 15th Space Simulation Conference, Williamsburg, VA, October (1988).
7. Moore, A.W., Strong, S.L., Doll, G.L., Dresselhaus, M.S., Spain, I.L., Bowers, C.W., Issi, J.P., Piraux, L., Properties and Characterization of Codeposited Boron Nitride and Carbon Materials, J. Appl. Phys., Vol 65, No. 12, 1989, pp 5109-5118.
8. Hedin, Alan E., "MSIS-86 Thermospheric Model," J. Geophysical Research, Vol 92, No. A5, 1987, pp 4649-4662.
9. Rutledge, Sharon K., Banks, Bruce A., DiFilippo, Frank, Brady, Joyce, Dever, Therese, and Hotes, Deborah, An Evaluation of Candidate Oxidation Resistant Materials for Space Applications in LEO, NASA TM-100122, November 1986.

Unexposed

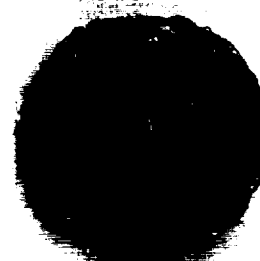
Exposed



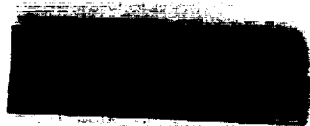
PG



HOPG



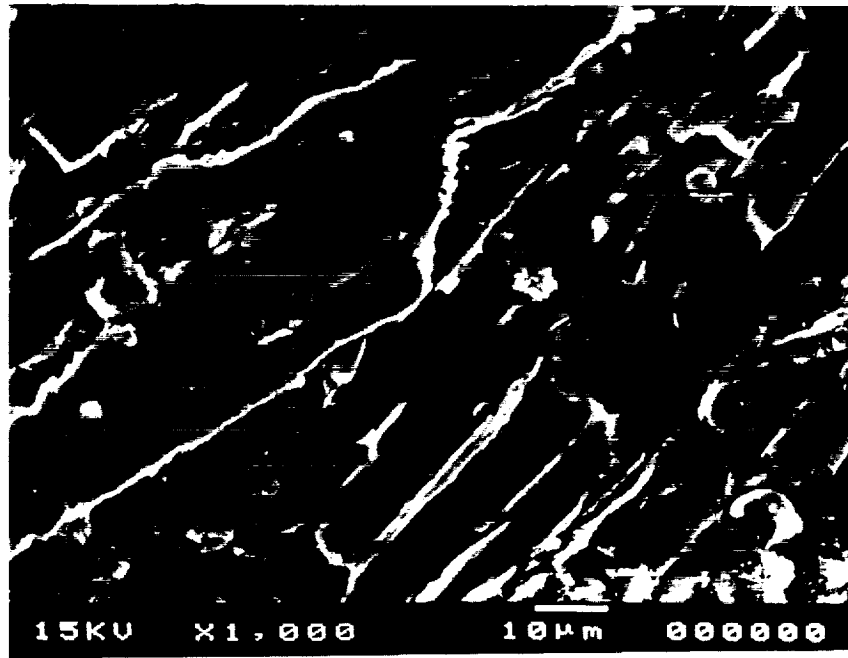
Gas Infiltrated
C/C Composite



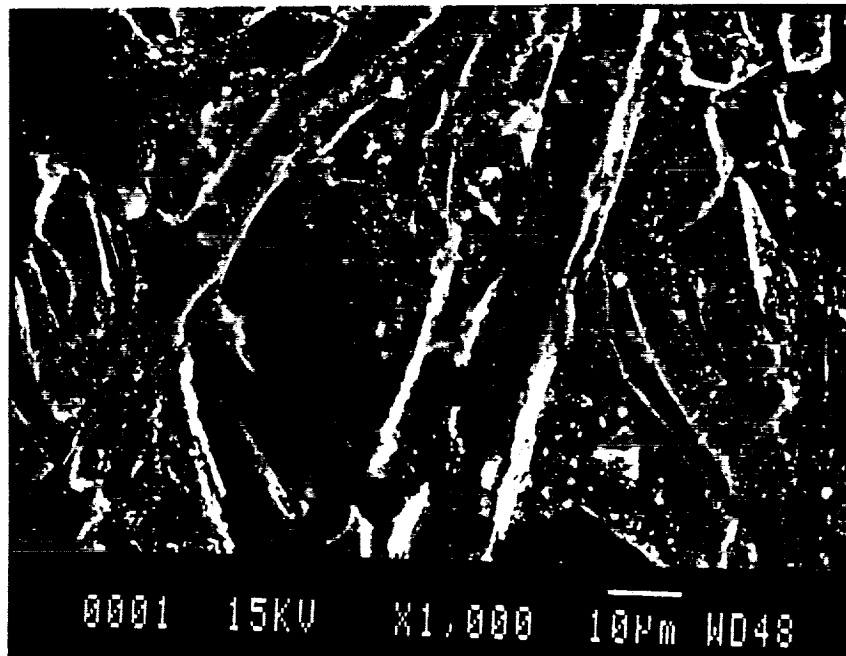
Liquid Infiltrated
C/C Composite



Figure 1. Visible degradation of samples after LEO exposure.



Unexposed



Exposed

Figure 2. SEM images showing preferential etching of graphite binder in the liquid infiltrated C/C composite.

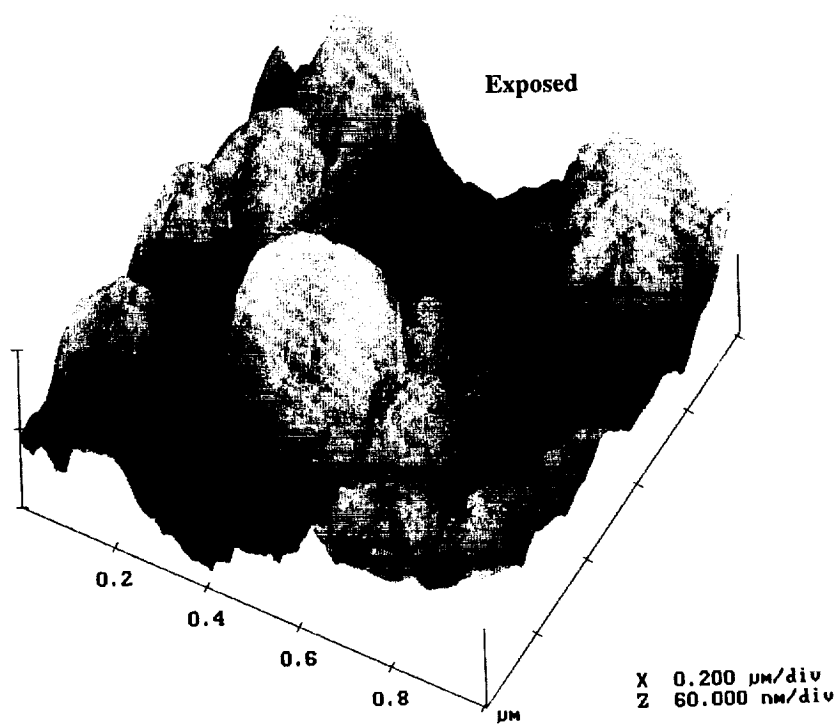
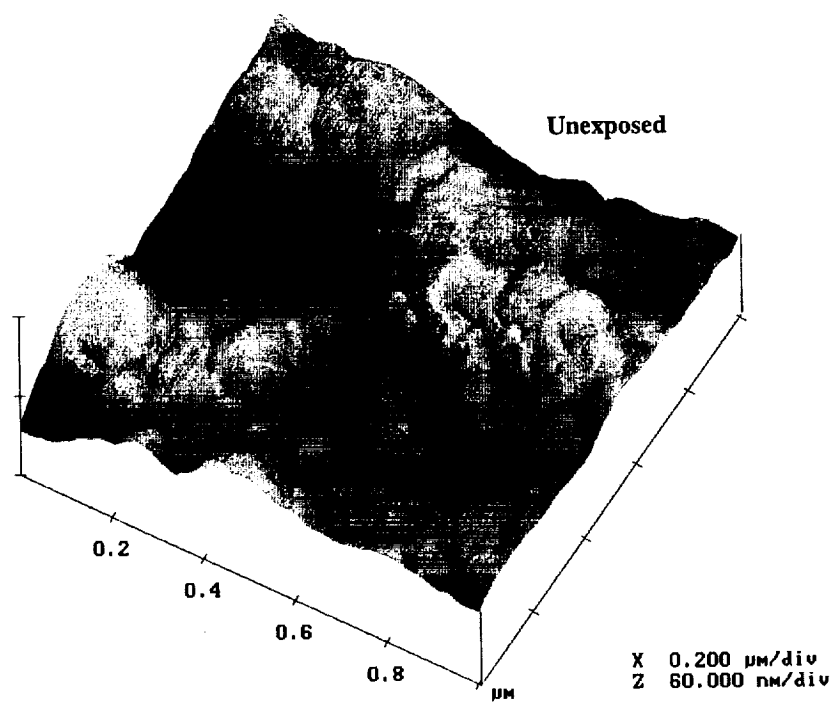


Figure 3. AFM data showing preferential etching of graphite domains in 60% C-BN.

